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Thermodynamic properties of associating chain molecules

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Abstract : When a molecule has two or more anisotropic attraction sites, chain ring and tree-like cluster can form. The fraction of clusters of a given size can be estimated using purely statistical arguments. The effect of molecular associations on the attractive centers is investigated. Such a system's thermodynamic properties can be calculated by using expressions based on a theory recently proposed by Wertheim. The approach is extended to examine associating chain molecules. In this study, the separate effects of molecular and chain size on the coexistence properties are investigated.

Keywords : Associating chain molecules, compressibility.

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1. Introduction

The development of analytical expression for strongly associating fluids has proved to be difficult problem, whereas fairly simple theories provide a good description of non polar and weakly polar fluids. Hydrogen bonding and charge transfer are cases of such chemical associations between molecules.

A more promising route leading to an understanding of associating fluids which are firmly based in Statistical Mechanics. One approach is to introduce the possibility of molecular association into commonly used integral equation theories. Thus Cumming and Stell [1] have solved the Percus-Yevick (PY) approximation for the chemical association by using a spherical symmetric bonding potential. The highly directional hydrogen bonding is introduced in fluids by the geometry of the interaction at an early stage of the theory. As a starting point for simple fluids, the cluster expansion is introduced in terms of the total singlet number density ρ. The effect is cumbersome and inefficient in such an expansion of the number density and the strength of hydrogen bond. Since in Andersen's model the attractive site is short ranged and highly directional the repulsive cores will restrict the system to single bond at each attractive site. Chandler and Pratt have developed the ideas of physical cluster to study spherically symmetric bonds of chemical strength, like Andersen [2,3], Wertheim [4,5] introduces the geometry of the interaction at an early stage. Wertheim's theory, however, is based on a resumed cluster expansion which is made in terms of two densities, the total number density ρ, and the monomer density ρ_0. In so doing, the correct low density limit for the second virial coefficient is guaranteed as well as providing an accurate representation of the extent of dimerization for liquid like densities. Wertheim was able to simply the complex graphical expansions by assuming that the repulsive core of each molecule restricts the orientationally dependent attractive forces to only single bond at each attractive site. The final expression can be written in the form of a thermodynamic perturbation theory which is relatively simple to use.

After viewing the complexity of all these theories, one is struck by the simplicity and elegance of Wertheim's theory [6–8] and it is this approach that has been extended to determine the thermodynamic properties of hard sphere molecules with highly directional attractive sites per molecules.

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2. Basic theory

(a) Potential model :

We consider a model, short range, highly anisotropic attractions, between the associating molecules, of chemical bonding such a hydrogen bond. The pairwise additive two body potential is given by

$$u(12) = u_R(12) + \sum_A \sum_B (r_{AB}) \tag{1}$$

where

$$r_{AB} = r_2 + d_B(\omega_2) - r_1 - d_A(\omega_1)$$

is a vector connecting site A on molecules 1 with site B on molecules 2. Here r_i is the position vector of the centre of molecules i, ω_1, ω_2, is its orientation, and d_A is the vector from the molecular center to site A, $u_r(12)$ is the hard core repulsive portion of the potential.

$$u_r(12) = \infty \text{ if } r < \sigma,$$
$$= 0 \text{ if } r > \sigma. \tag{2}$$

The site-site interactions u_{AB} are assumed to be purely attractive. Here σ is the hard-sphere diameter, d_{site} is the distance of the attractive site from the sphere's center C, r_c is the cutoff distance of the attractive potential, and r_{AB} is the distance between the centers of the two sites. The square well site-site interaction is given by

$$u_{AB} = -\epsilon_{AB} \text{ if } |r_{AB}| \le r_c,$$
$$= 0 \text{ if } |r_{AB}| \ge r_c. \tag{3}$$

Hence, bonding occurs between two istes when they are within the cutoff distance r_c of each other. The potential model that has just been described is simple and seems to have all the qualitative features of the physical interactions between real molecules with anisotropic attractions. When the attraction sites A and B on molecules 1 and 2 respectively get sufficiently close to form a band, then the repulsive cores of molecules 1, 2 and 3 prevent molecules 3 coming close enough to form bond either site A or B.

(b) Perturbation :

Using thermodynamic pertubation theory, the hard-core repulsive potential as the reference system and M directional attractive sites as a perturbation the excess free energy between the associating fluid and the reference fluid (A_{bond}) is given by

$$(A_{bond})/NkT = (\ln X_A - X_A/2) + M/2, \tag{4}$$

where X_A is the fraction of molecules not bonded at site A, N is the number of molecules, T is the temperature and k is Boltzmann's constant. The individual X_A are obtained from the mass-action eq. (9).

$$X_A = 1 + \sum \rho X_A \Delta_{AB} \tag{5}$$

where ρ is the total number dinsity. The Δ_{AB} is defined by

$$\Delta_{AB} = \int g_R(12)\, f_{AB}(12)\, d(12). \tag{6}$$

Here, $g_R(12)$ is the reference fluid pair correlation function. The Mayer f-function is

$$f_{AB}(12) = \exp(-u_{AB}(r_{AB})/kT) - 1 \tag{7}$$

and $d(12)$ denotes an unweighted average over all orentations and an integration over all separation of moleccules 1 and 2. Thus, the properties of the associating fluid can be calculated if one knows the pair distribution function of the hard core reference fluid. In the case of hard-sphere reference fluid, expression [4] for Δ_{AB} can be written in the form

$$\Delta_{AB} = 4\pi \int g_{HS}(12) < F_{AB}(12) >_{\omega_1\omega_2} r_{12}^2 d(12). \tag{8}$$

For the system with one square-well bonding site Wertheim showed that

$$< F_{AB}(12) >_{\omega_1\omega_2} = F_{AB} \{ (r_c - 2d_{site} - r_{12})^2$$
$$\times (2r_c - 2d_{site} + r_{12}) / 24 d_{site}^2 r_{12} \}, \tag{9}$$

where $F_{AB} = \exp(\epsilon_{AB}/kT)$-1 for the square well site-site interacions. Than eq. (9) reduces to

$$\left[\{ < F_{AB}(12) >_{\omega_1\omega_2} \} / F_{AB} \right] = \{ (r_c - 2d_{site} - r_{12})^2$$
$$\times 2r_c - 2d_{site} + r_{12}) / 24 d_{site}^2 r_{12} \}$$

and

$$K_{AB} = \sigma^2 \int_{\sigma}^{r_c + d_{site}} \left(< f_{AB}(12) >_{\omega_1\omega_2} / F_{AB} \right) dr_{12} \tag{10}$$

$$= \sigma^2 \left[\ln((r_c + 2d_{site})/\sigma) \left(6r_c^3 + 18 r_c^2 d_{site} - 24 d_{site}^3 \right) \right.$$

$$+ (r_c + 2d_{site} - \sigma)\left(22d_{site}^2 - 5r_c d_{site} - 7d_{site}\sigma\right.$$

$$\left. - 8r_c^2 + r_c\sigma + \sigma^2\right)\Big] 72d_{site}^2. \quad (11)$$

The value of Δ_{AB} for the hard-sphere reference system, we assume that $r_{12}^2 g_{HS}(r_{12})$ is constnat and equal to the value at contact $\sigma^2 g_{HS}(\sigma)$ over the short range of the site-site potential. This appears to be a reasonable approximation for the system which can be modeled by highly directional and short ranged potential such as hydrogen bonds. Thus, eq. (8) reduces to

$$\Delta_{AB} = 4\pi\sigma^2 g_{HS}(\sigma) \int < f_{AB}(12) >_{\omega_1\omega_2} d_{12}. \quad (12)$$

The equilibrium constant Δ_{AB} is evaluated using eqs. (8) and (11) in the approximate form

$$\Delta_{AB} = 4\pi g_{HS}(\sigma).K_{AB}.F_{AB}, \quad (13)$$

where $g_{HS}(\sigma)$ is the contact value of the pair distribution function of the hard-core reference fluid in the Carnahan-Starling approximation

$$g_{HS} = (1 - \eta/2)/(1 - \eta)^3. \quad (14)$$

The quantity K_{AB} is a measure of the volume available for bonding on every molecules. In particular, the size of the bonding volume K_{AB} is a function of molecular diameter.

The expression given by [10] for the chain fluids is an analogue of a Flory-Huggins lattice theory for continuous space. The equation of state for a pure fluid of homonuclear hard-sphere chain is given by

$$Z_{HC} = Z_{HS} + Z_{Chain}. \quad (15)$$

The pure hard-sphere compressibility factor Z_{HS} is given by the equation of Carnahan and Starling :

$$Z_{HS} = (1 + \eta + \eta^2 - \eta^3)/(1 - \eta)^3, \quad (16)$$

where $\eta = (\pi\rho\sigma^3)/6$ is the packing fraction. Z_{Chain} for chains made up of m hard sphere is obtained as

$$Z_{Chain} = (m - 1)/m[1 + \rho\{\partial(\ln g_{HS}(\sigma)/\partial\rho\}]. \quad (17)$$

In the form of Carnahan and Starling, the hard chain compressibility facotor becomes [10,11]

$$Z_{HC} = Z_{HS} + Z_{Chain}$$

$$= (1 + \eta + \eta^2 - \eta^3)/(1 - \eta)^3,$$

$$- [\{(m - 1)/m.\{(1 + \eta + \eta^2/2)(1 - \eta)(1 - \eta/2)], \quad (18)$$

where m is the number of sphere in the chain and η is the packing fraction. The compressibility factors of the hard-sphere chain are expressed in terms of the total number of spheres in the system.

3. Associating fluid of chain molecules

For molecules with only one attractive site, $X = X_A$ is the fraction of monomers and $1 - X$ is the fraction of molecules present as dimers. When a molecule has two or more anisotropic attraction site, chain, ring and tree-like clusters can form. Although theory does not give us direct information on the distribution of clusters, the fraction of clusters of a given size can be estimated using purely statistical arguments. The system with two bonding sites, A and B, the system can bind to form chains and rings of any length. The general theory for associating molecules with multiple attraction sites have now been presented. In this paper we consider fluids with one or two directional attraction sites. A hard sphere system is chosen as the reference. For a pure fluid of associating chain molecules, the compressibility factor is a sum of the separate contributions, with

$$Z = Z_{HC} + Z_{MF} + Z_{bond}. \quad (19)$$

The hard-chain repulsive term Z_{HC} for homonuclear chains of m sphere is as eq. (18) and the mean field contribution is

$$Z_{MF} = - \varepsilon_{MF} \eta/kT, \quad (20)$$

where the constant ε_{MF} is measure of the strength of the mean-field forces. The reduced density of spheres in the chains is used to calculate the mean field contribution. For a one component chain fluid with M attractive sites, the change in compressibility factor due to association [12] is

$$Z_{bond} = \eta(\partial X/\partial\eta)_{T,N} (1/X) - (1/2)). \quad (21)$$

For a system with one bonding site, X is given by

$$X = 1/1(1 + \rho\Delta_{AB}X) \quad (22)$$

and for positive root

$$X = [-1 + \sqrt{(1 + 4\rho\Delta_{AB})}]/2\rho\Delta_{AB}. \quad (23)$$

Fro two component chain fluids with M attractive sites,

the change in the compressibility facotr due to association is

$$Z_{bond} = 2\eta(\partial X/\partial\eta)_{TN}\ (1/X - 1/2)). \quad (24)$$

This expression appears to be twice the result obtained for the system with one bonding site. however, here X_A represents the fraction of molecules not bonded at site A, which is different from the fraction of monomers X_A is determined from the equation

$$X_A = 1/(1 + \rho\Delta_{AB}X) \quad (25)$$

and by solving the quadratic equation with $X_A = X_B$, we have

$$X_A = [-1 + \sqrt{(1 + 4\rho\Delta_{AB})}]/2\rho\Delta_{AB}. \quad (26)$$

We now have the expression to calculate the thermodynamic properties of associating chain fluids with one or two square well attractive sites.

4. Results and discussion

It is important to determine the adequacy of eq. (18) in predicting the thermodynamic properties of homonuclear chains of hard spheres for a chains of different fixed lengths 2, 4, 6, 8, 12, 16. A compression of the hard-chain reference equation with the computer simulation results for various chain length of Dickman and Hall [13], excellent agreement is found for low number of spheres of chains as shown in Figure 1. The value of compressibility factor increases with increase of reduced density and for large number of spheres in chain solidification started. For low number of spheres the calculated value of compressibility factor agree with computer simulation results.

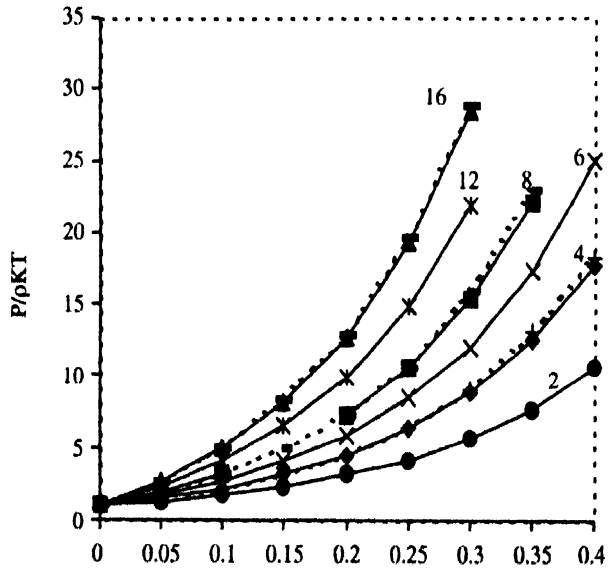

Figure 1. The compressibility factor ($P/\rho\ kT$) for chains of different fixed length. The dot points represent the values for Dickman and Hall and solid curves represent present result.

In Figure 2, we reported the bonding volume K_{AB} as a function of ε_{site} at constant σ with $r_c = 1.05\sigma$. The graph is plotted against ε_{site}. We found that for small value of ε_{site}, the value of bonding volume for formation of bond is maximum.

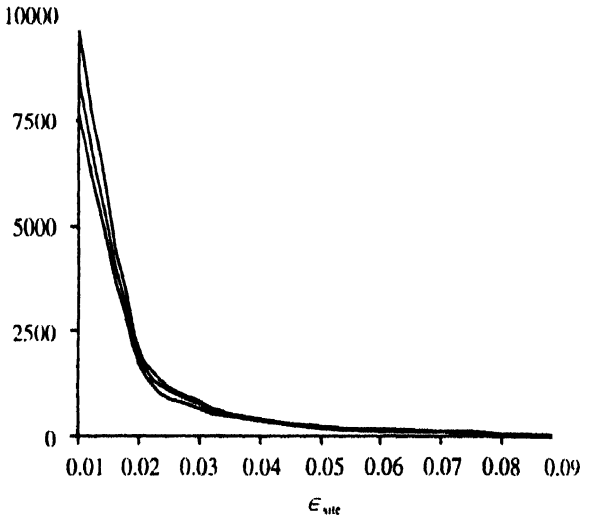

Figure 2. The quantity K_{AB} is a measure of the volume available for bonding on every molecule at constant $r_c = 1.5\sigma$ as function on ϵ_{site}.

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